

EXPOSURE OF AGRICULTURAL EMPLOYEES TO
1,2-DICHLOROPROPANE AND 1,3-DICHLOROPROPENE
(TELONE AND DD) IN CALIFORNIA, 1983

by

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SUMMARY

Employees performing pre-plant soil fumigations were monitored for exposure to the fumigants Telone and DD. Inhalation exposures to Telone (1,3-dichloropropene) and DD (1,3-dichloropropene, 1,2-dichloropropene mixture) were measured with air samples. Eight-hour time-weighted average (TWA) inhalation exposures to 1,2-dichloropropene (1,2-D) ranged from 0.003 to 0.44 ppm, with a mean of 0.17 ppm. Eight-hour TWA inhalation exposures to 1,3-dichloropropene (1,3-D) ranged from 0.07 to 3.61 ppm, with a mean of 0.71 ppm. 1,2-D and 1,3-D residues on the hands were monitored with hand washes. 1,2-D was not detected on the hands; in some samples, low microgram residues of 1,3-D were detected. It is doubtful, however, that these measurements accurately represent skin exposures to fumigants. The efficiency of half-face respirators was measured with inside-mask air samples collected from specially plumbed respirators. In these studies, half-face respirators provided greater than a 10-fold reduction in inhalation exposure. 1,2-D and 1,3-D exposures were generally below exposure standards recommended by the American Conference of Governmental Industrial Hygienists (ACGIH). However, employers should take steps to reduce exposures pending evaluations of the potential carcinogenic hazards posed by these fumigants.

INTRODUCTION

Cis- and trans-1,3-dichloropropene and 1,2-dichloropropane are halogenated hydrocarbons which have been used in soil for several years to control plant-parasitic nematodes (1). These compounds are components of the pre-plant soil fumigants Telone (Dow Chemical Company, 92 percent 1,3-D) and DD (Shell Chemical Company, 50 percent 1,3-D and 30 percent 1,2-D). Telone and DD are used as pre-plant soil treatments for nematode control in numerous field crops, in vineyards, and in orchards. Annual use of these fumigants in California from 1977 to 1982 has increased from 10 million to 16 million pounds, with 1981 being a peak use year (2).

The ACGIH recommend a Threshold Limit Value (TLV) of one ppm for 1,3-D based on an eight-hour TWA and a short-term exposure limit (STEL) of 10 ppm (3). 1,3-D has been identified as mutagenic in microbial assays (4,5), and has been studied for possible carcinogenicity in a National Toxicology Program (NTP) animal bioassay (NTP contract number 542-75-6). The data from this study is currently under peer review and has not received final verification by the NTP. The ACGIH recommends a TLV of 75 ppm for 1,2-D based on an eight-hour TWA and an STEL of 110 ppm, though they suggested that the TLV be reduced to a level corresponding to other hepatotoxic halogenated hydrocarbons (3). 1,2-D has also been identified as a microbial mutagen, though at doses 500-fold greater than 1,3-D (4). 1,2-D has also been studied for possible carcinogenicity in an animal bioassay; however, the results have not yet been verified by the NTP. The concerns of Department toxicologists about the potential carcinogenicity of these compounds initiated this exposure study of fumigant applicators.

Soil fumigation normally involves injecting liquid fumigant approximately six inches into the soil through tubing attached to a set of shanks. The shanks are mounted on a tool bar attached to either a wheeled or tracklaying tractor. The treated soil is sealed by a roller or cultipacker drawn by the fumigant rig or a second tractor. The fumigant is loaded into the tractor tanks from a nurse tank stationed at the edge of the field. Loading is performed through closed systems utilizing quick-disconnect, dry-break couplers, and gasoline or electric powered pumps. During loading operations, the tractor tanks are vented to open air several feet away from the employee, into an injection shank or back into the nurse tank. Depending on the number and capacity of the tractor tanks, and the application rates, fumigant loads are performed every 45 minutes to two hours of application time. The actual loading process requires 5 to 15 minutes.

Applicators commonly wore one-piece cloth coveralls and leather work boots while driving the tractor. Rubber boots, neoprene or rubber gloves, a plastic apron and a half-face respirator with organic vapor cartridges were donned prior to loading fumigants.

Telone and DD applications were studied in the San Joaquin Valley, coastal areas of Santa Cruz County, and the Salinas Valley. In the San Joaquin Valley there are two seasons of peak use, in the spring

and fall, each lasting from four to six weeks. During these seasons, applicators work five to six days a week, usually 12 hours a day. Very little soil fumigation occurs outside the peak seasons. Most fumigants are applied to fallow ground prior to planting beans, sweet potatoes, cotton, sugarbeets, stone fruit, and grapes. Along the coast and in the Salinas Valley, fumigant applications occur throughout much of the year, except for a few winter months when the soil is too wet. The applicators' work schedules are more sporadic, and work days of eight hours (or less) are more common. Most applications take place in fallow ground prior to planting broccoli, Brussels sprouts, cabbage, carrots, cauliflower, celery, and lettuce.

Telone application rates vary with crop and soil type, but commonly range from five to fifteen gallons per acre (gpa); up to 40 gpa will be applied prior to establishing vineyards or orchards. DD application rates commonly range from 15 to 40 gpa, with up to 60 gpa for vineyards and orchards.

MATERIALS AND METHODS

Pest control operators located in Merced, Monterey, Santa Cruz, and Stanislaus Counties were cooperators in this study. Employee inhalation exposures to 1,2-D and 1,3-D were evaluated using air sampling. Air samples were drawn from employee breathing zones (BZ) using charcoal sorbent tubes and battery powered air pumps (see Appendix One for sampling methods and equipment). Eight-hour TWA exposure levels were calculated from partial period samples covering from 30 to 80 percent of an employee's workday. In the Merced County studies, separate BZ samples were drawn for loading (or repair) operations and applications (tractor driving). Elsewhere, fumigant exposures from all facets of the operation were integrated into one sample. Short-term exposures were monitored during loading or repair operations in Monterey, Santa Cruz and Stanislaus Counties with a "surrogate loader" technique. One or more investigators, outfitted with air samplers (and half-face respirators), would stand near the employee (two to six feet away), monitoring the fumigant concentrations in the employee's vicinity during loading or repair operations.

The effectiveness of the half-face respirator in reducing inhalation exposure of 1,3-D was evaluated using the "surrogate loader" technique. An investigator was outfitted with a plumbed half-face respirator and two air samples were drawn, one sampling air inside the respirator and the other sampling the outside air.

Skin exposure was monitored using hand wash sampling with distilled water and surfactant (6). These samples were collected prior to and following loading and repair operations (see Appendix Two for sampling methods).

All samples were stored on ice until delivery to the chemist. The chemical analyses were performed by the Department's Chemistry Laboratory Services in Sacramento. Each sample was analyzed for 1,3-D and

selected samples were also analyzed for 1,2-D with gas chromatography. (Sample preparation and analytical methods are in Appendices One and Two.)

Employee BZ measurements were converted to eight-hour TWA exposures (see Table One for an example of the TWA calculation). The length of the unsampled period was based on the judgments of the investigators, using practices outlined in OSHA Industrial Hygiene Field Operations Manual (7). These judgments were based on work place observations, estimations of the treatment rate (approximately six acres per hour), acreages scheduled for treatment that day, and interviews with the employees. TWA exposures were calculated for employees in the coastal areas (Santa Cruz and Monterey Counties) based on eight-hour workdays. TWA exposures for employees in the San Joaquin Valley (Stanislaus and Merced Counties) were based on 12-hour work days. Mean values and 95 percent confidence intervals were calculated for the populations of TWA values (8,9).

RESULTS

The eight-hour TWA exposures of applicators to 1,3-D ranged from 0.09 to 3.61 ppm; the arithmetic mean was 0.71 ppm. The eight-hour TWA exposures of applicators to 1,2-D ranged from 0.003 to 0.44 ppm; the arithmetic mean was 0.17 ppm. These data, and the 95 percent confidence intervals of the means are in Table One. 1,3-D and 1,2-D TWA exposures during each application are listed in Table Two. BZ samples drawn during loading operations (in Merced and Stanislaus Counties) detected 1,3-D concentrations ranging from 0.06 to 42 ppm. These results are listed in Table Three. Comparisons of ambient and inside-respirator 1,3-D concentrations are in Table Four. Half-face respirators appeared to provide greater than a ten-fold reduction over ambient 1,3-D concentrations during loading or repair operations; these are listed in Table Five. Thirty-five (35) of 37 surrogate loader measurements detected 1,3-D concentrations less than 5.0 ppm. Six (6) of 28 hand wash measurements detected 1,3-D residues, ranging from one to 23 micrograms per sample (see Table Six).

DISCUSSION

TWA inhalation exposures of applicators to 1,3-D generally did not exceed 1.0 ppm. During 3 of 21 applications monitored, employee TWA exposures exceeded 1.0 ppm (see Table 2A). Loading operations have previously been considered the greatest potential sources of 1,3-D exposure (10). It is presently not possible to evaluate this based on the employee exposure measurements made during loading operations (see Table Three). However, the low concentrations in most of these samples (2.0 ppm, or less, of 1,3-D) and the small portion of the day spent loading fumigant (10 to 15 percent of an eight-hour day) indicates that this operation may not provide a large contribution to an employee's TWA exposure. Inhalation exposures probably occur from spilled fumigant volatilizing from equipment surfaces or from treated soil, or from

liquid fumigant draining onto the soil while the shanks were out of the soil. Shanks are out of the soil while fumigant is being loaded, during repairs, or as the tractor turns around at the edge of the field. Concentrations of 1,3-D volatilizing from freshly treated soil have been reported between 0.2 and 0.5 ppm (11).

A closed-system malfunction occurred during one application, releasing approximately two liters of Telone onto the ground. A BZ sample from a loader drawn during this operation, contained 42 ppm of 1,3-D. At a different application, during a fumigant load, an employee accidentally over-filled the tractor tank and spilled Telone out of the vent tube. A surrogate loader sample monitoring this activity contained 2.0 ppm 1,3-D. The employee's TWA exposure was 3.61 ppm. Repairs to the fumigation equipment were monitored with the surrogate loader technique at a third application. A 1,3-D concentration of 8.5 ppm was detected in the work area; the employee's TWA exposure was 0.92 ppm. The dry-break couplers routinely spilled droplets or splashes of liquid fumigant when uncoupled. This liquid release usually did not splash on the employee, in the applications monitored, but could serve as sources of inhalation exposure.

The surrogate loader technique was used to minimize interference with the employee's activities. This type of sampling technique has not been considered the best technique for evaluating employee exposures to a contaminant; BZ sampling is considered more appropriate (8,12). However, these results indicate that work place concentrations of 1,3-D, while loading fumigants, generally remain below 5.0 ppm. Work place concentrations of 1,3-D can greatly exceed 5.0 ppm in the event of a closed system malfunction, or extensive repairs to the fumigation equipment.

Concentrations of 1,2-D detected in employee BZ samples generally did not exceed 0.5 ppm. Air and hand wash samples were not routinely analyzed for 1,2-D in this study. A relatively small number of applicators were monitored, so some uncertainty exists about how clearly these results characterize the exposures of most fumigant applicators to 1,2-D.

Measurements of hand exposure, made during loading operations, did not reveal substantial 1,3-D residues on the skin (ranging from 1.0 to 23.0 micrograms). This was possibly due to careful handling of liquid fumigant, use of gloves and rapid volatilization of 1,3-D residues from the skin. During a few applications, the investigators observed small spills onto gloves or equipment surfaces, which would evaporate to dryness within a few minutes. Aqueous hand washes probably do not efficiently remove 1,3-D residues from the skin. Also, a few minutes would elapse from when the employee finished his task, allowing time for 1,3-D residues to evaporate from the skin prior to sampling. High levels of dermal exposure to 1,3-D were observed during two applications, with liquid fumigant wetting the hands to the point of run-off. These were associated with a field man calibrating fumigation equipment and an applicator performing repairs, both employees neglecting to use gloves.

These studies, and others performed by the Department, indicate that respiratory exposure to 1,3-D can be reduced with the use of half-face respirators with organic vapor cartridges (13). However, they do not allow conclusions about the effects of respirator use for any particular employer. The effectiveness of respiratory protection devices depends on the employer establishing a program to support respirator use.

Inhalation exposures to 1,2-D and 1,3-D during the applications monitored were generally below the TLV's recommended by the ACGIH; however, it is not certain that the recommended values protect employees from potential carcinogenic hazards. Assessments of the carcinogenic hazards await completion of the NTP cancer bioassays. Until the hazards of exposure to 1,2-D and 1,3-D can be assessed, employers should take all steps possible to minimize employee exposures. Pest control operators handling volatile fumigants should establish respiratory protection programs, or evaluate the effectiveness of existing programs. Employee training should be periodically conducted on the proper use of gloves and respiratory protective equipment. Fumigation equipment should be routinely serviced to reduce the need for in-field maintenance (which places the employee away from decontamination facilities and emergency first aid care) and reduce the potential for accidental release of fumigant from ruptured hoses or leaking fittings. Fumigant concentrations over treated soil can be influenced by soil preparation (14,15). Proper soil moisture and tilth can seal the applied fumigant into the soil, reducing airborne concentrations and employee exposure. Pest control advisers should encourage soil preparation practices which will reduce off-gassing fumigant vapors following application.

CONCLUSIONS

1. The average eight-hour TWA inhalation exposure of employees loading and applying 1,2-dichloropropane was 0.17 ppm. The range of TWA exposures was from 0.003 to 0.44 ppm.
2. The average TWA inhalation exposure of employees loading and applying 1,3-dichloropropene was 0.71 ppm. The range of TWA exposures was 0.07 to 3.61 ppm.
3. Fumigant loading operations did not appear to provide large contributions to employee TWA exposures to 1,2-D or 1,3-D. However, high concentrations of 1,3-D (exceeding 5 ppm) in the work place were associated with sizable releases of liquid fumigant from spills or leaking equipment.
4. A respiratory protection program, incorporating the use of approved respirators, can substantially reduce inhalation exposure to 1,2-D and 1,3-D.
5. Skin exposure to 1,3-D, as measured on the hands, was small. This may be due to safe handling and the high vapor pressure of the compound. However, the sampling technique in this study may not adequately measure fumigant residues on the hands.

6. Pending a complete evaluation of the potential carcinogenic hazards, employers should take steps to minimize employee exposures to 1,2-D and 1,3-D.

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Table 1

EIGHT-HOUR TWA EXPOSURES OF EMPLOYEES APPLYING DD OR TELONE^{a/}

Chemical	Number of Applications Monitored	Concentration of Fumigant (ppm)		95% Confidence Interval of the Mean
		Range	Arithmetic Mean	
1,3-dichloropropene	21	0.07 - 3.61	0.71	0.55 - 0.87
1,2-dichloropropane	5	0.003 - 0.44	0.17	Not Determined ^{b/}

^{a/} TWA exposures calculated with the following formula:

$$TWA = \frac{C_1 T_1 + C_2 T_2 + C_3 T_3 + \dots + C_n T_n}{8 \text{ hours}}$$

Where C = ppm detected and T = sample duration in hours.

^{b/} Value is too small compared to the TLV to compute a meaningful confidence interval.

Exposure during the portion of the work day when fumigation is not performed is considered zero.

Table 2

Eight-Hour TWA Exposures of Employees Applying
Telone or DD to 1,3-Dichloropropene or 1,2-Dichloropropane

<u>County</u>	<u>Date</u>	<u>Pesticide</u>	<u>Concentration of Fumigant (ppm)</u>	
			<u>1,3-D</u>	<u>1,2-D</u>
Monterey	5/04/83	Telone	0.57	-- ^{a/}
	5/05/83	Telone	3.61	--
	5/11/83	Telone	0.91	--
	5/24/83	DD	0.23	NA ^{b/}
	5/25/83	DD	1.10	NA
	5/26/83	DD	0.86	NA
	6/09/83	Telone	0.11	--
	6/16/83	DD	0.43	0.10
Santa Cruz	6/08/83	DD	0.24	NA
	6/10/83	DD	0.08	NA
Stanislaus	4/07/83	Telone	1.15	--
	4/08/83	Telone	0.92	--
	4/19/83	Telone	0.92	--
	4/20/83	Telone	0.29	--
	5/11/83	Telone	0.07	--
	5/12/83	Telone	0.46	--
Merced	4/06/83	DD	0.28	NA
	4/12/83	DD	0.28	0.09
	4/12/83	DD	0.62	0.44
	4/13/83	DD	0.79	0.003
	4/13/83	DD	1.30	0.24

^{a/} 1,2-D analyses were not performed on Telone samples.

^{b/} NA means not available.

Table 2A

Distribution of 1,3-Dichloropropene TWA Exposures

<u>Range of 1,3-D Concentrations (ppm)</u>	<u>Number of TWA Exposures Within the Concentration Range</u>
ND ^{a/} to 0.19	3
0.20 to 0.39	5
0.40 to 0.59	3
0.60 to 0.79	2
0.80 to 0.99	4
1.00 to 1.19	2
1.20 to 3.61	2
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Total	21

^{a/} ND means none detected, minimum detectable level 0.002 ppm.

Table 3

Short-Term Employee Exposures to 1,3-Dichloropropene and
1,2-Dichloropropane During Loading Operations

<u>Date</u>	<u>Pesticide</u>	<u>County</u>	<u>Sampling Duration (min.)</u>	<u>Concentration of Fumigant (ppm)</u>	
				<u>1,3-D</u>	<u>1,2-D</u>
4/06/83	DD	Merced	13	0.38	NA ^{a/}
4/06/83	DD	Merced	16	1.17	NA
4/06/83	DD	Merced	16	0.96	0.11
4/12/83	DD	Merced	8	0.97	0.70
4/12/83	DD	Merced	19	0.06	NA
4/12/83	DD	Merced	14	0.26	ND ^{b/}
4/13/83	DD	Merced	14	1.28	0.83
4/13/83	DD	Merced	11	2.05	0.03
4/13/83	DD	Merced	9	0.11	ND
4/13/83	DD	Merced	11	0.42	ND
5/12/84	Telone	Stanislaus	14	41.9	NA

^{a/} NA means not available.

^{b/} ND means none detected, minimum detectable level is 0.003 ppm.

TABLE 4

Comparisons of Ambient Concentrations With
Inside-Respirator Concentrations of 1,3-Dichloropropene

<u>County</u>	<u>Date Sampled</u>	<u>Ambient Concentration (ppm)</u>	<u>Inside-Respirator Concentration (ppm)</u>	<u>Calculated Protection Factor</u>
Monterey	5/04/83	0.03	ND ^{a/}	15
		0.57	0.01	57
		1.45	0.04	145
	5/05/83	1.98	ND	990
	5/10/83	0.04	ND	20
	5/11/83	0.37	ND	185
		0.13	ND	65
		0.79	ND	395
Santa Cruz	5/25/83	0.02	ND	10
		0.78	0.02	39
	5/26/83	1.32	ND	660
	5/24/83	0.56	0.01	56
		0.32	0.01	32
Monterey	6/16/83	0.04	ND	20
Mean		0.60	0.008	
Standard Deviation		0.61	0.011	

Mean Protection Factor: 192

Standard Deviation: 294

Range of Protection Factors

Low: 10

High: 990

^{a/} ND means none detected, minimum detectable level (MDL) is 0.002 ppm. The MDL is used as the inside-respirator concentration for calculation of the protection factor.

Short-Term Measurements of 1,3-D and 1,2-D Concentrations
in the Work Place During Loading or Repair Operations

Table 5
("Surrogate Loader" Samples)

County	Date	Pesticide	Sampling Time (min.)	Fumigant Concentration (ppm)	
				1,3-D	1,2-D
Monterey	5/04/83	Telone	10	0.03	-- ^{a/}
			11	0.57	--
			9	1.45	--
Monterey	5/05/83	Telone	10	1.98	--
Monterey	5/11/83	Telone	12	0.37	--
			8	0.13	--
			9	0.79	--
Monterey	6/09/83	Telone	11	ND ^{b/}	--
Monterey	6/16/83	Telone	6	0.04	0.03
Monterey	5/25/83	DD	16	0.02	NA ^{c/}
			16	0.02	NA
			8	1.04	NA
			8	0.78	NA
			8	0.16	NA
Monterey	5/26/83	DD	8	1.32	NA
			8		
Santa Cruz	6/10/83	DD	9	0.48	NA
			9	0.04	NA
Monterey	5/24/83	DD	10	0.56	NA
			10	0.32	NA
Santa Cruz	6/08/83	DD	10	ND	NA
Stanislaus	4/07/83	Telone	10	4.07	--
			7	8.52	--
Stanislaus	4/08/83	Telone	7	4.72	--
			25	1.36	--
			6	0.08	--
			8	3.14	--
Stanislaus	4/20/83	Telone	17	0.62	--
			17	0.63	--
			12	0.57	--
			12	0.12	--
			13	1.19	--
Stanislaus	4/20/83	Telone	13	21.7	--
			8	3.49	--
			8	2.68	--
			14	0.71	--
			14	0.34	--
Stanislaus	5/11/83	Telone	14	12.1	--
			14		

^{a/} 1,2-D analyses not performed on Telone samples.

^{b/} Means none detected, minimum detectable level is 0.002 ppm.

^{c/} Sample not available, or analysis not performed.

Table 5A

Distribution of 1,3-Dichloropropene Concentrations
Measured in the Work Place During Loading or Repair Operations

<u>Range of 1,3-D Concentrations (ppm)</u>	<u>Number of Measurements Within the Concentration Range</u>
ND ^{a/} to 0.19	11
0.20 to 0.59	7
0.60 to 0.99	5
1.00 to 5.00	11
Greater than 5.00	3
Total	37

^{a/} ND means none detected, minimum detectable level is 0.02 ppm.

Table 6

Residues of 1,3-D and 1,2-D Detected
on the Hands of Employees Loading Telone or DD

<u>County</u>	<u>Date</u>	<u>Pesticide</u>	<u>Residues of 1,3-D Detected (ug)</u>		<u>Residues of 1,2-D Detected (ug)</u>	
			<u>Pre-load</u>	<u>Post-load</u>	<u>Pre-load</u>	<u>Post-load</u>
Monterey	5/11/83	Telone	ND ^{a/}	ND	-- ^{b/}	--
			ND	ND	--	--
			NA	ND	--	--
	5/24/83	DD	ND	ND	NA ^{c/}	NA
			NA	ND	NA	NA
	5/25/83	DD	ND	ND	NA	NA
			ND	ND	NA	NA
			ND	ND	NA	NA
			ND	ND	NA	NA
Stanislaus	4/19/83	Telone	ND	10.2	--	--
			ND	1.0	--	--
	4/20/83		23.0	12.2	--	--
			ND	10.2	--	--
	5/11/83		0.9	ND	--	--
	5/12/83		ND	7.4	--	--
Merced	4/06/83	DD	1.6	ND	ND ^{c/}	ND
			NA	5.4	NA	NA
			1.7	1.9	ND	ND
			NA	2.1	NA	ND
	4/12/82	DD ^{d/}	NA	2.4	NA	ND
			22.0	ND	ND	ND
			2.2	7.2	ND	ND
			NA	ND	NA	ND
			NA	3.9	NA	ND
			NA	ND	NA	ND
			NA	1.0	NA	ND
			NA	3.1	NA	ND
			NA	ND	NA	ND

Number of 1,2-D samples: 16

Number of 1,3-D samples: 44

Number with detectable residues: 18

Range of 1,3-D residues (micrograms): 1.0 to 23.0

No 1,2-D residues detected

^{a/}No 1,3-D detected, minimum detectable level is 0.3 ug.

^{b/}1,2-D analyses not performed on Telone samples.

^{c/}Sample not available, or analysis not performed.

^{d/}No 1,2-D detected, minimum detectable level is 1.0 ug.

^{e/}Data combined from two applications.

Table 7

Characteristics of the Telone and DD Applications Monitored in 1983

<u>Date</u>	<u>County</u>	<u>Crop</u>	<u>Pesticide</u>	<u>Application Rate (gal/ac)</u>	<u>Acreage Treated</u>
4/06/83	Merced	--	DD	--	--
4/07/83	Stanislaus	Tomatoes	Telone	4.5	--
4/08/83	Stanislaus	Tomatoes	Telone	4.5	--
4/12/83	Merced	--	DD	--	--
4/12/83	Merced	Sweet Potatoes	DD	24	--
4/13/83	Merced	Sweet Potatoes	DD	25	--
4/13/84	Merced	--	DD	--	--
4/19/83	Stanislaus	Grapes	Telone	20	17
4/20/83	Stanislaus	Grapes	Telone	20	17
5/04/83	Monterey	Broccoli	Telone	6	95
5/05/83	Monterey	Broccoli	Telone	8	87
5/11/83	Monterey	Broccoli	Telone	8	50
5/11/83	Stanislaus	Beans	Telone	--	--
5/12/83	Stanislaus	Beans	Telone	--	--
5/24/83	Monterey	--	DD	16	40
5/25/83	Monterey	--	DD	16	--
5/26/83	Monterey	--	DD	16	20
6/08/83	Santa Cruz	Brussels Sprouts	DD	15	35
6/09/83	Monterey	--	Telone	6	12
6/10/83	Santa Cruz	Brussels Sprouts	DD	12	25
6/16/83	Monterey	Broccoli	DD	7	29

The Sampling of 1,2-Dichloropropane and
1,3-Dichloropropane in Air

Scope:

This method is for the collection of 1,2-dichloropropane and isomers of 1,3-dichloropropane (Telone and DD) from air into charcoal sampling tubes. It is intended solely for the use of the California Department of Food and Agriculture, Worker Health and Safety Unit.

Equipment:

1. Charcoal sorbent sampling tubes--SKC, Inc. #226-09.
2. Personal sampling pump, MSA Model S or TD, calibrated to draw one liter per minute across the sorbent bed.
3. Tygon tubing, 1/4 inch, i.d. Sufficient length to position sampling tube in employee's breathing zone (BZ).
4. Binder clips or safety pins, to affix sampling tube to the lapel (within the BZ).
5. Leather belt, men's large size.
6. Kurz Model 540S flow calibrator.
7. Glass bottles, ice chest and ice, for sample storage.

Methods:

1. Assemble sampling train. Connect Tygon tubing to pump. Break tips off of a sampling tube and insert into open end of the Tygon tubing, ensuring that the direction-of-air-flow arrow on the tube, points towards the pump.
2. Calibrate sampling pump flow at one liter per minute, drawing air across the sorbent bed, with the Kurz flow calibrator.
3. Clip the sampling pump to the employee's belt. If coveralls are being worn, supply the employee with a belt.
4. Start the sampling pump; note the starting time.
5. At the end of the sampling period, remove the sample from the employee, recalibrate the sampling pump flow with the Kurz calibrator, stop the pump, note the stop time.
6. Cap the exposed sampling tube with the supplied plastic caps. Label the sampling tube.

7. Store the tube in the glass jar and chill on ice. Periodically supply a blank tube, handled like the exposed tubes but with no air drawn through it, to determine any interference in the batch of charcoal tubes.

References:

Anonymous. NIOSH Manual of Analytical Methods, 2nd Edition. Ethylene Dibromide, Method S104 (1977).

Written By:

John Lowe, Environmental Hazards Specialist
December 16, 1983

Determination of 1,2-Dichloropropane and
1,3-Dichloropropene on Charcoal Tubes

Scope:

This method is for the desorption and analysis of Telone II from charcoal air sampling tubes. It is intended solely for the use of the California Department of Food and Agriculture, Chemistry Laboratory Services.

Principle:

Telone II that has been collected from the air onto activated charcoal is desorbed from the charcoal with ethyl acetate, diluted as needed and analytically determined by gas chromatography using electron capture detection.

Reagents and Equipment:

1. Ethyl Acetate, nanograde.
2. Analytical Grade Telone II -- 1,3-dichloropropene. Analytical grade 1,2-dichloropropane.
3. Approved and calibrated personal sampling pump.
4. Charcoal tubes -- SK #226-09.
5. Developing vials with teflon lines -- SKC #226-02.
6. Assorted microsyringes for preparing standards and gas chromatography.
7. Assorted pipets.
8. Volumetric flasks.
9. Small triangular file for scoring glass tubes.

Analysis:

Interferences: High humidity may affect trapping efficiency.

1. Score each charcoal tube with a file in front of the first section of charcoal.
2. Break open the tube. Remove and discard the glass wool.
3. Transfer the charcoal in the upstream section to a labeled desorption vial, and add a known amount of nanograde ethyl acetate; 2-4 ml is suggested.

4. Remove, then discard the foam partition from the tube.
5. Transfer the second section of charcoal to a second labeled desorption vial, and add a known amount of nanograde ethyl acetate.
6. Allow the samples to desorb for one hour on the rotator.
7. Transfer an aliquot to a sample storage vial, label, and freeze until analysis time.
8. Determine by GLC.

Determination of Desorption Efficiency:

1. Remove the foam and second section of charcoal from a charcoal tube of the same lot number used for the determinations.

Inject a known amount of 1,2-dichloropropane or 1,3-dichloropropene (one to several hundred micrograms) into the charcoal with a syringe and cap the tube with the supplied caps.

At least five tubes (preferably at levels covering the expected range) should be prepared in this manner and allowed to stand at least overnight to assure complete adsorption. A blank tube should be treated the same way except that no sample is added.

Analyze the tubes by the analytical procedure.

$$\text{Desorption efficiency} = \frac{\text{Response sample} - \text{response blank}}{\text{Response standard}}$$

The standard is the same amount as injected into the charcoal tubes.

Calculations:

1. Determine weight of 1,3-dichloropropene present on charcoal tube sections by GLC analysis. Nanograms or micrograms are most convenient.
2. Correct this total weight of 1,3-dichloropropene by subtracting any blank value present on the blank tube.
3. The corrected weight is divided by the desorption efficiency to obtain the final weight of 1,3-dichloropropene present.
4. The volume of air sampled is converted to standard conditions of 25°C and 760 mm Hg. Use of the Kurz 540S flow calibrator provides a correction to standard conditions.

$$VS = \frac{V \times P \times 298}{760 \times (T+273)}$$

Where VS = Volume of air at standard conditions.
V = Volume of air as measured.
P = Barometric pressure in mm Hg.
T = Temperature of air in °C.

5. Calculate ppb in air from the above data.

$$\text{ppb (volume basis)} = \frac{\text{ng} \times 24.45}{VS \times 111.0}$$

24.45 is the mole volume of 1,3-dichloropropene at 25° and 760 mm.

111.0 is the molecular weight of 1,3-dichloropropene.

The calculations are identical for 1,2-dichloropropane, except the molecular weight is 113.0.

Gas Chromatographic Conditions:

1,3-Dichloropropene:

Instrument: Varian 3700 with ⁶³Ni electron capture detector.

Column: 12 ft. x 2 mm i.d. glass column packed with 10% SP-2100 coated on 100/120 mesh Chromasorb W-HP, operated at 60°C and 20 ml/min N₂ carrier gas.

Injector: On-column injection at 200°C.

Detector: Set conditions according to manufacturer's specifications.
Detector temperature: 300°C. Under these conditions, the 1,3-D peaks elute at 4.7 and 5.3 minutes.

1,2-Dichloropropane

Instrument: Varian 3700 with Tracor HECD (Hall Electroconductivity Detector).

Column: 20 ft. x 1/8 in. i.d. nickel column packed with 10% SP-2100 on 100/120 Chromosorb W-HP operated at 50°C and 20 ml/min He carrier gas.

Detector: Set conditions according to manufacturer's specifications.
Detector temperature: 300°C.

References:

- NIOSH Manual of Analytical Methods, Second Edition. Method S104.
Available from Superintendent of Documents, U.S. Government
Printing Office, Washington, D.C., 20402.
- Determination of EDB in Crops, Soil, Water, Bark, and Leaves, California
Department of Food and Agriculture, Chemistry Laboratory Services,
1220 N Street, Sacramento, California 95814.
- Determination of EDB on Charcoal Tubes, California Department of Food
and Agriculture, Chemistry Laboratory Services, 1220 N Street,
Sacramento, California 95814.
- Zweig, G., Analytical Methods for Pesticides on Plant Growth Regulators
VI, 710, 1972.

Written By:

A. Scott Fredrickson, Agricultural Chemist II
April 16, 1979

Determination of 1,3-Dichloropropene
Residues on the Hands

Scope

This method is for the collection and determination of 1,3-dichloropropene residues on the hands. The principle is rinsing the hands in a water/surfactant solution, then analyzing this rinsate for 1,3-dichloropropene residues with gas chromatography. This method is intended solely for the use of the California Department of Food and Agriculture, Worker Health and Safety Unit.

Equipment:

1. 16 oz. glass jars and screw caps.
2. Freezer size polyethylene "Ziploc" bags.
3. 16 oz. water/surfactant solution. Prepared by dissolving 0.05 percent (w/w) surten (70 percent dioctylsulfosuccinate sodium salt) in distilled water. 16 oz. is sufficient to collect a single hand wash sample.
4. Aluminum foil.
5. Paper towels.
6. Ice chest and ice.

Methods:

Hand wash samples are collected at the discretion of the investigator. Best use for this sampling technique is for work procedures that may bring an employee in contact with traces of liquid fumigant.

1. Prior to starting the task (fumigant loading or repairs), have the employee wash his hands in the manner specified below.
2. Prepare hand wash solution by pouring 16 oz. of water/surfactant solution into a Ziploc bag.
3. Collect sample by inserting employee's hands, one at a time, into the bag and shaking hand approximately 10 seconds. Provide employee with paper towels.
4. Quickly transfer the solution to a tall glass jar, and seal with foil and a screw cap.
5. After the employee completes his task, collect a second hand wash sample, repeating steps 2 through 4.

6. Store samples on ice.

Discussion:

The rationale underlying this method is that the initial sample removes any previous residues from the hands, while the final sample measures how much residue is deposited on the hands after performing the task. The efficiency of this method for removing residues from hands has not been determined. Errors in determination of skin residues can be introduced from, even temporarily, storing the hand wash solution in the polyethylene bags. Problems exist in quantitating the amount of fumigant residues on the hands; since they are volatile, fumigant deposits probably fluctuate rapidly. Losses can occur from the hands by volatilization, from the moment an employee completes his task, to the moment the sample is collected. Further development is recommended to determine appropriate methods for sampling volatile pesticides from the skin.

References:

Davis, J. E., Minimizing Occupational Exposure to Pesticides: Personnel Monitoring. Residue Reviews. 75:34-50 (1980).

Noel, M. E., G. Zweig and W. J. Popendorf: Evaluation of the Cotton Glove and Hand wash Technique for Measuring Dermal Exposure to Field-workers. Presented at the 185th National Meeting of the American Chemical Society, Seattle, Washington. March 20-25, 1983.

Written by:

John Lowe, Environmental Hazards Specialist
December 16, 1983

Analysis of 1,3-Dichloropropene in Hand Wash Samples

Scope

This method is for the desorption and analysis of 1,3-dichloropropene from hand wash samples. It is intended solely for the use of the California Department of Food and Agriculture, Chemistry Laboratory Services.

Principle

A suitable size sample is codistilled with ethyl acetate. The recovered ethyl acetate (plus any 1,3-dichloropropene from sample) is dried with sodium sulfate and determined quantitatively through the use of gas-liquid chromatography with electron capture detector.

Equipment

1. Balance, sensitive to 10 mg.
2. Distillation receiver - Barrett trap 25 ml capacity with S 24/40 joints.
3. Heating mantle controlled by variable transformer. 500 ml boiling flask capacity.
4. 500 ml flat or round bottomed boiling flask with S 24/40 joints. (If many bark or leaf samples are to be run, it may be desirable to substitute a larger joint such as S 45/40 with adapters to S 24/40.)
5. Condenser, Allihn type: 250 to 300 jacket with S 24/40 lower joint and drip tip.
6. Glass stoppered test tubes or auto sampler vials fitted with Teflon faced septa for holding samples.
7. Pipette, 10 ml T.D. or 10 ml repipet.
8. Syringes, assorted microliter syringes for injection on gas chromatograph. Suggested sizes 1, 5, and 10 microliter.

Reagents

1. Analytical Standard of 1,3-Dichloropropene.
 - a. Stock Standard - Prepare 1 mg/ml in ethyl acetate.
 - b. Working Standards - Dilute stock standard to several working standards covering the linear range of specific e.c. detector used. Typically in the range of 0.02 - 1.0 nanogram/microliter.

- c. Ethyl Acetate - Nanograde or better. Test for interferences before use.
- d. Acetone - Nanograde or better for pre-rinsing and drying equipment.
- e. Anhydrous Sodium Sulfate, Granular. Suggest Mallinkrodt. Pretest for interferences. Ethyl acetate wash or heat in muffle furnace if interferences are found. If interferences are not removed, use sulfate from a different source.
- f. Antifoam - Silicone antifoam agent for organics or mixed aqueous and organics.

Note: Use only if absolutely necessary. Will depress recovery of 1,3-dichloropropene.

- g. Distilled Water - Good quality, distilled water stored in glass. Test water with a reagent blank for extraneous peaks and large solvent front.

Note: It has been necessary to pre-extract water using the outlined codistillation method in order to remove materials interfering with the GLC analysis.

Procedure

Sample Distillation:

1. Measure and record amount of solution.
2. Weigh sample into boiling flask. (200 ml of water sample.)
3. Add exactly 10.0 ml of ethyl acetate. If experience has indicated that sample will foam uncontrollably, add 1 drop of antifoam. If antifoam is used, the recoveries must be rechecked with antifoam in the fortified samples.
4. Place the boiling flask into the heating mantle and assemble the Barrett trap and condenser (with flowing water) in place.
5. Apply full voltage to heating mantle until mixture starts to boil (approximately 5 to 7 minutes), then reduce voltage to 1/4 to 1/2 and allow to reflux for 15 minutes.
6. Check graduations on Barrett trap to determine if all of the ethyl acetate has been distilled over. If it hasn't, continue refluxing in 5-minute intervals, otherwise, remove heat from flask and wash down condenser and trap neck with a few milliliters of distilled water. Let cool (approximately 5 minutes).

7. Drain off lower aqueous layer from trap and discard.
8. Drain ethyl acetate layer into glass stoppered test tube for analysis.

Sample Clean-Up and Analysis:

1. Add a small amount of sodium sulfate to the test tube and shake well to remove entrapped water.

Note: We normally attempt to match standards in peak height and area to the peak height and area of 1,3-D peak in samples.

3. Gas Chromatography - See Appendix One for chromatographic conditions.

Calculations

Calculations must reflect the fact that only an aliquot was analyzed. Results are reported in microgram per total sample, and the total amount of hand wash solution should be noted.

Written by:

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December 16, 1983